Experimental Verification of the Gapless Point in the $S=1$ Antiferromagnetic Bond Alternating Chain

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Abstract

Susceptibility and high field magnetization measurements have been performed on powder samples of an $S=1$ bond alternating chain compound $[\{Ni(333\text{-tet})(\mu\text{-}N_3)\}_n](ClO_4)_n$ (333-tet=tetraamine N,N'-bis(3-aminopropyl)-1,3-propanediamine). As the temperature is decreased, the susceptibility exhibits a round maximum at around 120 K and decreases gradually down to 10 K, and then falls down rapidly with a logarithmic curvature which is behavior of the susceptibility of a gapless or a nearly gapless antiferromagnetic chain. Magnetization up to 50 T at 1.4 K shows no or a very small gap in this compound. We have carried out numerical calculations for the $S=1$ antiferromagnetic bond alternating chain with various alternating ratios α and obtained a very good agreement between experiments and calculations for α=0.6. We verify experimentally that the gapless point exists around α=0.6.

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Experimental and theoretical efforts on low dimensional magnetic systems have brought about a profound understanding of physics in many body quantum systems. In particular, linear chain Heisenberg antiferromagnets (LCHA's) with the quantum spin number $S=1$ have been studied extensively [1–3] in connection with Haldane's conjecture [4] that there is an energy gap between the ground state and the first excited one for integer S, while not for half-odd integer S. Recently, low dimensional oxide systems, such as inorganic spin-Peierls systems [5,6] and spin ladder systems [7,8], have attracted a lot of interest.

One of the recent interesting topics in $S=1$ LCHA's is bond alternation. Using the Hamiltonian for the $S=1$ bond alternating chain given by $\mathcal{H} = \sum_i \{1 - (-1)^i \delta\} \mathbf{S}_i \cdot \mathbf{S}_{i+1}$ where δ ($0 \leq \delta \leq 1$) is the parameter representing bond alternation and $\mathbf{S}_i$, $\mathbf{S}_{i+1}$ $S=1$ spin operators, Affleck and Haldane [9] predicted that there is a massless (gapless) point at a certain alternating ratio δ_c. Subsequent numerical studies [10–15] estimated the critical ratio δ_c as 0.25. Moreover, it was shown numerically that the ground state is in the Haldane or the singlet dimer phase depending on δ ($0.0 \leq \delta < 0.25$ for the former and $0.25 < \delta \leq 1.0$ for the latter).

In the recent years, some Ni bond alternating compounds [16–19] were synthesized and the magnetic properties were studied. They were (a) $catena$-[$\{Ni_2(\mu$ -$N_3)_3(dpt)_2\}_n$]$(ClO_4)_n$ (dpt=bis(3-aminopropyl)amine), (b) $\{Ni_2(EDTA)(H_2O)_4\}_n \cdot (2H_2O)_n$ (EDTA= ethylene-diaminetetraacetic acid), (c) $trans$-[$\{Ni(333$-tet$)(\mu$-$N_3)\}_n$]$(ClO_4)_n$ (333-tet= N,N'-bis(3-aminopropyl)-1,3-propanediamine), (d) [$\{Ni_2(dpt)_2(\mu$-ox$)(\mu$-$N_3)\}_n$]$(PF_6)_n$ (ox=C_2O_4), and (e) [$\{Ni_2(Medpt)_2(\mu$-ox$)(\mu$-$N_3)\}_n$]$(ClO_4)_n$ (Medpt=methyl-bis(3-aminopropyl)amine). Alternating ratios α of the neighboring exchange constants were obtained from the fit of the susceptibility to a formula calculated by Borrás-Almenar [20] using the Hamiltonian defined as,

$$\mathcal{H} = J \sum_{i=1}^{N/2} (\mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i} + \alpha \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1}). \tag{1}$$

However, no comparison between experiment and theory have been carried out from the viewpoint of verification of the phase separation and the gapless point. Note that the

critical ratio α_c corresponding to δ_c is 0.6. Magnetization curves at zero Kelvin of the $S=1$ LCHA with bond alternation were calculated with the Hamiltonian $\mathcal{H} = \sum_i [\{1 - (-1)^i \delta\} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + g\mu_B S_i^z H + D(S_i^z)^2]$ where $g\mu_B S_i^z H$ is the Zeeman term, g the g value of Ni^{2+}, μ_B the Bohr magneton and H the external magnetic field, and $D\sum_i (S_i^z)^2$ is the single ion anisotropy term [21]. One of the important features in this study is that a 1/2-plateau appears in the magnetization curve at least when $0 < \delta \leq 1$ and $D \geq 0.0$. Quite recently, the above finding was generalized and it was argued that the magnetization per site m is topologically quantized as $n(S - m)$ =integer at the plateaus, where n is the period of the ground state [22]. Accordingly, in the $S=1$ antiferromagnetic bond alternating chain ($n = 2$), $m=1/2$ can be quantized in addition to $m=0$ and 1. Under such circumstances, some of the authors performed magnetization measurements on some of these compounds and observed 1/2-plateaus in magnetization curves of $\{Ni_2(EDTA)(H_2O)_4\}_n \cdot (2H_2O)_n$ and $[\{Ni_2(Medpt)_2(\mu\text{-ox})(\mu\text{-N}_3)\}_n](ClO_4)_n$ [**?**].

In the present paper, we report the results of susceptibility and high field magnetization measurements performed on powder samples of $[\{Ni(333\text{-tet})(\mu\text{ -N}_3)\}_n](ClO_4)_n$. We have found that the experimental results shows no or a very small gap in this compound and verified that α_c should be about 0.6 in comparison with some numerical results.

First, we mention the synthesis and the crystal structure of $[\{Ni(333\text{-tet})(\mu\text{ -}N_3)\}_n](ClO_4)_n$. The compound $[\{Ni(333\text{-tet})(\mu\text{ -N}_3)\}_n](ClO_4)_n$ was synthesized with a slow evaporation method from an aqueous solution containing equimolars of $Ni(ClO_4)\cdot 6H_2O$, 333-tet ligand and NaN_3 according to ref. [18]. This compound crystallizes in the triclinic system, space group $P\bar{1}$. The lattice constants and angles at room temperature are $a=8.765(1)$Å, $b=8.976(1)$Å, $c=11.995(2)$Å, $\alpha=106.65(1)°$, $\beta=110.06(1)°$ and $\gamma=91.11(1)°$. Each Ni atom is placed in an octahedral environment and links to the neighboring Ni atoms via azido (N_3) groups to form the chain structure along the c axis. The chain structure of this compound is shown in Fig. 1. Here, most of the ligand atoms and the counter anions ClO_4^- are omitted for simplicity. The neighboring chains are well separated from each other by ClO_4^- anions. Two kinds of alternating centrosymmetric azido bridges are present in the chain. The Ni-N

bond distances and Ni-N-N bond angles for these azido bridges are 2.077(3)Å, 142.4(3)°
and 2.204(3)Å, 123.6(2)°, respectively, giving bond alternation in the chain. Susceptibility
(M/H) was measured at 100 Oe with SQUID magnetometer (Quantum Design's MPMS2)
in RIKEN and high field magnetization measurements were done with a pulsed magnet up
to 50 T at KYOKUGEN in Osaka University.

Susceptibility of the powder sample of $[\{Ni(333\text{-tet})(\mu\text{-}N_3)\}_n](ClO_4)_n$ is shown in Fig. 2.
A round maximum appears around 120 K and the susceptibility decreases gradually down to
10 K, and then it decreases steeply as the temperature is decreased further. No long range
order was observed down to 1.8 K. Low temperature part (below about 30 K) of the suscepti-
bility is quite similar to that of the $S=1/2$ LCHA which was calculated recently by the Bethe
ansatz and a field theory methods [24] and observed experimentally in an organic ion radical
salt [3,3'-dimethyl-2,2'-thiazolinocyanine]-TCNQ [25]. From the similarity of these findings,
we can say that this system is gapless or nearly gapless because of a logarithmic fall down
in the susceptibility at low temperatures [26]. We compare the susceptibility with some nu-
merical calculations (an exact diagonalization method and a quantum Monte Carlo (QMC)
method (loop algorithm) [27]) for the Hamiltonian (1), including the single ion anisotropy
term for the former case. In the former calculation, the susceptibilities at and around the
gapless points predicted in the D versus α plane [21] are calculated and compared with the
experimental one. Then, we conclude that the susceptibility can be fitted for a small D/J
(<0.1), α around 0.6 and $J/k_B \sim 100$ K. This small D/J is reasonable, because Ni^{2+} ion
under an octahedral ligand field usually has the D/k_B value varying from 1 K to 10 K. For
$D/k_BT \ll 1$, the susceptibility for a powder sample can be compared with the calculated
one for $D=0$. In Fig. 2, open squares show the results of the QMC method for 96 sites
with $\alpha=0.6$. The exchange constant J/k_B is estimated to be 110 K with the g value of 2.46.
The agreement between experiment and calculation is very good. We show α dependence
of the susceptibilities calculated by means of the QMC method (96 sites) in Fig. 3. Here,
we take the exchange constants and the g values to fit the experimental data at around 300

K. The susceptibilities except for α=0.6 decrease exponentially at low temperatures. It is easily mentioned from the calculated susceptibilities that the critical alternating ratio which corresponds to the gapless point exists around 0.6. Details and further results of the Monte Carlo calculation will be presented in a longer paper [28].

In order to confirm that this is a gapless or a nearly gapless system, we carried out high field magnetization measurements. The result is shown in Fig.4 together with the result of a numerical calculation at zero Kelvin made by the product-wave-function renormalization-group (PWFRG) method [29]. The PWFRG method has been verified [30] to be more useful for investigation of the magnetization process than the original density-matrix renormalization-group method devised by White [31]. The agreement between experiment and theory is also very good and the estimated exchange constant J/k_B is 115 K which is close to that obtained from the susceptibility fitting (110 K). In the inset of Fig.4, full magnetization curves up to the saturation field calculated by the PWFRG and a method introduced by Sakai and Takahashi (ST) [32] are shown, together with experimental data. According to the calculation, a 1/2 plateau of magnetization curve, which is characteristic of the S=1 bond alternating chains, should be expected around 140 T.

In conclusion, we have performed susceptibility and magnetization measurements on an S=1 antiferromagnetic bond alternating chain compound $[\{\mathrm{Ni}(333\text{-tet})(\mu\text{ -}N_3)\}_n](\mathrm{ClO_4})_n$. The susceptibility exhibits the behavior of a logarithmic fall down below 10 K, which is typical of the gapless antiferromagnetic chain. By comparing experimental results with some numerical calculations for the S=1 bond alternating chain with α=0.6, we have obtained a very good agreement and estimated the exchange constant J/k_B=110 $\sim$ 115 K and the g value of Ni^{2+} ion g=2.46. Consequently, we have verified experimentally that the gapless point exists around α=0.6.

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FIGURES

FIG. 1. Schematic view of the chain structure of $[\{\mathrm{Ni}(333\text{-tet})(\mu\text{ -N}_3)\}_n](\mathrm{ClO}_4)_n$. Most part of the 333-tet ligands and ClO_4^- anions are omitted for simplicity.

FIG. 2. Temperature dependence of the susceptibility (M/H) of a powder sample of $[\{\mathrm{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\mathrm{ClO}_4)_n$ (filled circles). Open squares show the calculated data by means of a quantum Monte Carlo (QMC) method for 96 sites for the $S{=}1$ bond alternating chain with the bond alternating ratio $\alpha{=}0.6$.

FIG. 3. Bond alternating ratio α dependence of the susceptibility calculated with a QMC method (96 sites).

FIG. 4. Magnetization of a powder sample of $[\{\mathrm{Ni}(333\text{-tet})(\mu\text{ -N}_3)\}_n](\mathrm{ClO}_4)_n$ at 1.4 K versus magnetic field up to 50 T. Broken line shows a magnetization curve at 0 K calculated with the product-wave-function renormalization-group (PWFRG) method. Inset: Calculated magnetization curves up to the saturation field by the PWFRG method (broken line) and a method introduced by Sakai and Takahashi (ST) (filled circles) , together with experimental data (solid line).
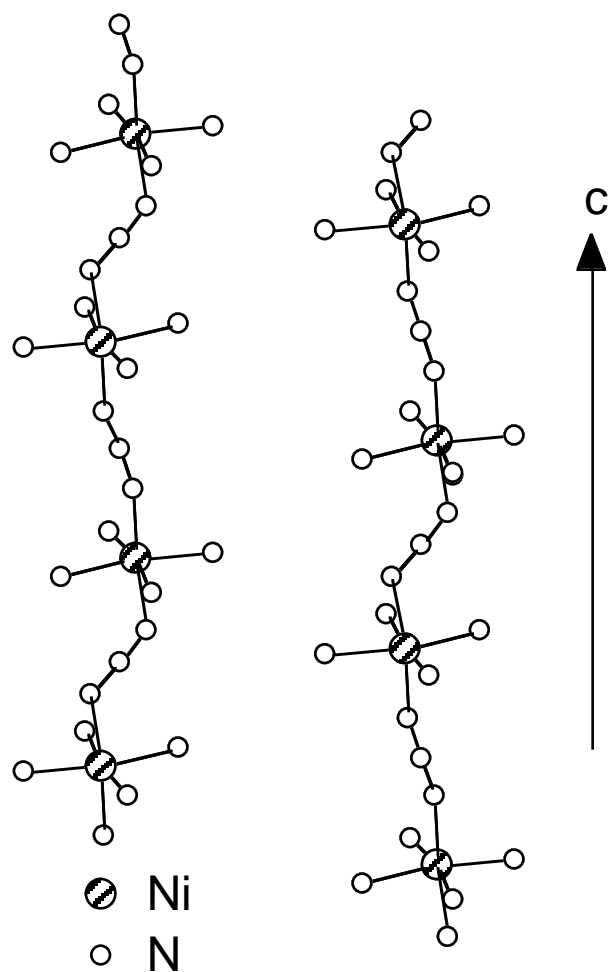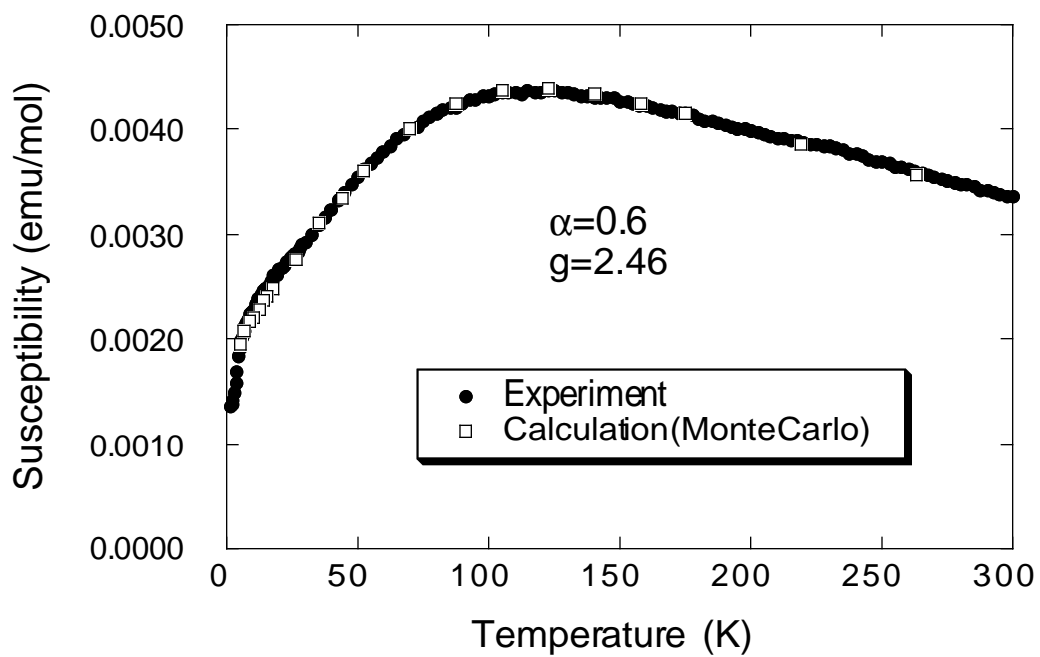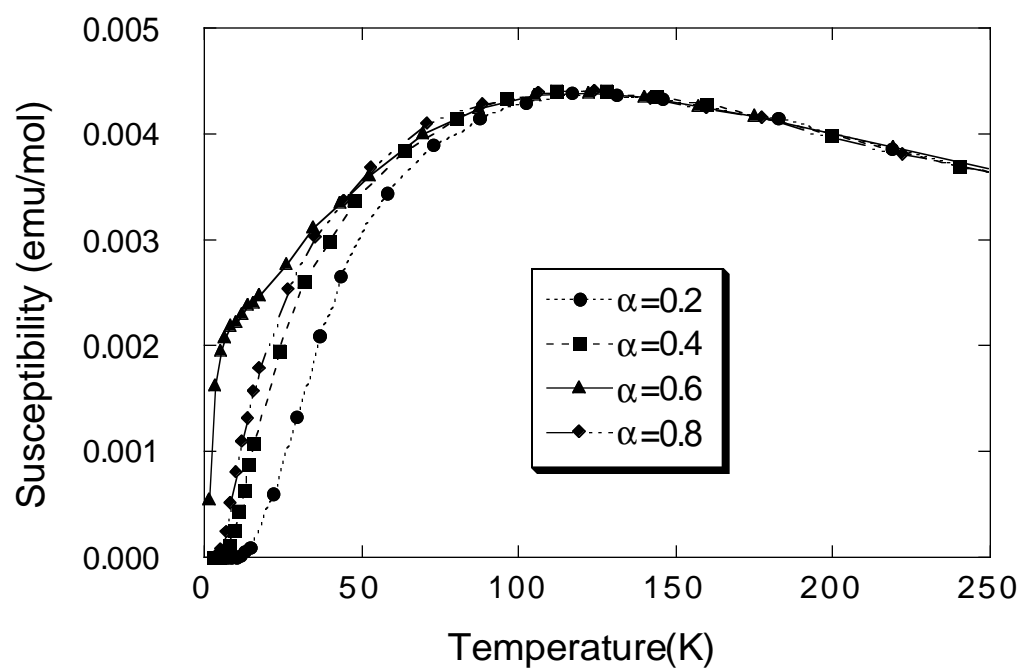
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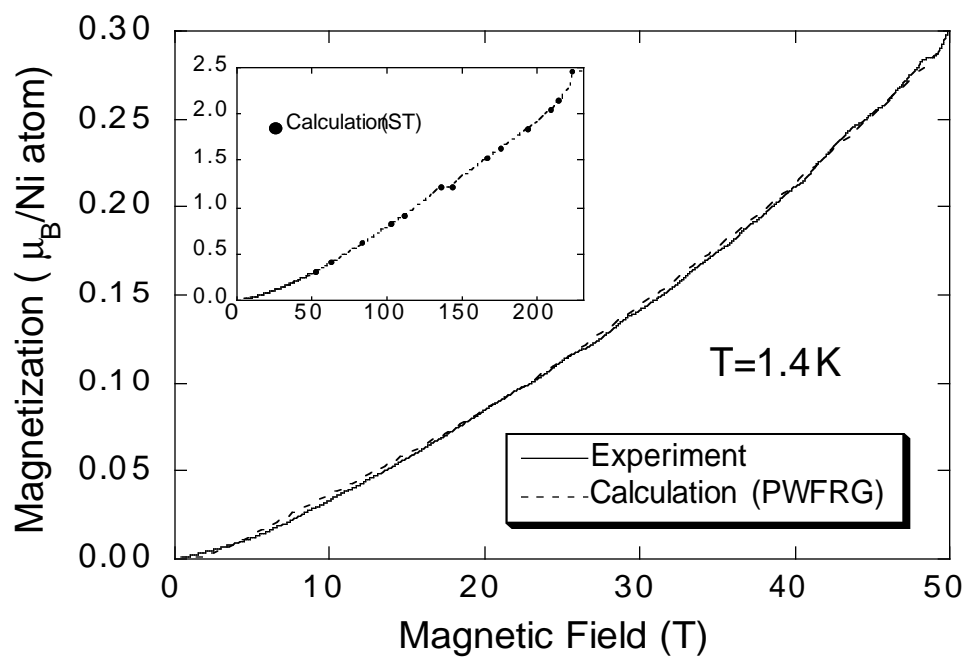
Fig.2 Hagiwara et al.

Fig.3 Hagiwara et al.

Fig.4 Hagiwara et al.